ZnS Nanoparticles as Novel Luminescent Probe to Detect Dissolved Oxygen

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Abstract

ZnS nanocrystrals are synthesized with oleylamine using zinc stearate and elemental sulfur as the precursors. Spherical ZnS nanoparticles (~2nm) were obtained and characterized using several different techniques (XRD, SEM, TEM). The long chain amines that are adsorbed on the surface of the particles were exchanged with 11-mercaptoundecanoic acid, making the ZnS nanoparticles water soluble. In water, ZnS nanoparticles have three distinct fluorescence peaks from 330 nm to 470 nm. The fluorescence lifetime ratio of ZnS nanoparticles is proportional to the dissolved oxygen concentration. Calibrating this relationship allows one to determine the concentration of dissolved oxygen in solution from 0 ppm to 20 ppm.

Keywords
Nanoparticles, fluorescence, lifetime, dissolved oxygen concentration

Introduction

In recent years, semiconductor nanoparticles, known as “quantum dots (QD)”, have attracted significant interests [1-3]. Because of their small size (typically from 1 to 10 nanometers), these materials display unique properties unlike the bulk materials, due to quantum size confinement effects, which occur when metal and semiconductor particles are smaller that their exciton Bohr radii. The quantum confinement makes non-fluorescing compounds develop an intense fluorescence emission. Compared with organic fluorescent dyes, the quantum dots exhibit important advantages, including large fluorescent quantum yields, tunable maximum wavelength of emission by controlling the QDs size [4] and less susceptible to photobleaching [5].

Many studies in this area focus on the development of new techniques to synthesize high-quality quantum dots with high-luminescent quantum yields. There is an increasing interest in the applications of such semiconductor nanoparticles as biomarkers in biological medicine and as probes in analytical chemistry. For example, it has been reported that CdSe nanoparticles incorporated into poly (methylmethacrylate) films were found to respond reversibly to amine in gaseous phase [6]. QDs have also been used as chemical sensing materials for determination of zinc and copper ions in aqueous media [7]. More recently, CdSe has been synthesized to detect inorganic anions e.g. CN^-, NO_3^-, Cl^-, SCN^-, and Br^- [8]. However, to our knowledge, the use of QDs to detect dissolved oxygen is unexplored. Because the photoluminescence of QDs arises from the recombination of excitons, it is reasonable to assume that dissolved oxygen will quench the photoluminescence of QDs. Oxygen is a unique molecule with a triplet state in the ground state [9], which is collectively denoted as $^3O_2$. When an oxygen molecule absorbs a certain amount of energy, the two electrons in the π^*_{2px} and π^*_{2py} orbitals will change to a singlet state with the electron spins opposite to each other, which by Hund’s rule has a higher energy.

A singlet excited state is created by exciting the lumophore with an excitation light source.

$$X_v + h\nu_{ex} \rightarrow X_c + heat \quad (1)$$

Here, X_v is the QDs in the valence band, $h\nu_{ex}$ are the photons at the excitation energy, and X_c is the conduction band.

There are several possible fates for X_c. One is for X_c to emit photons and return to the valence band. This process is called radiative decay.

$$X_c \overset{kr}{\rightarrow} X_v + h\nu_{em} \tag{2}$$

Another step is for the excited state to return to the valence band non-radiatively.

$$X_c \overset{kn}{\rightarrow} X_v + heat \tag{3}$$

When oxygen is present, energy from the excited state can be transferred non-radiatively to the oxygen, via a process known as quenching.

$$X_c + {}^3O_2 \overset{kq}{\rightarrow} X + {}^1O_2 + heat \tag{4}$$

The presence of oxygen in the system results in a more rapid depletion of the excited-state population, which is detected as a concomitant decrease in the steady-state luminescence intensity and a shorter emission decay time.

In this paper, ZnS nanocrystrals are synthesized with oleylamine using zinc stearate and elemental sulfur as the precursors. The long chain amines were exchanged with 11-mercaptoundecanoic acid, making the ZnS nanoparticles water soluble. In water, ZnS nanoparticles have three distinct fluorescence peaks from 330 nm to 470 nm. The fluorescence lifetime ratio of ZnS nanoparticles is proportional to the dissolved oxygen concentration. Calibrating this relationship allows one to determine the concentration of dissolved oxygen in solution.

2. Experimental

2.1 Materials and reagents

Hexadecylamine (HDA, 90%), oleylamine, sulfur powder, zinc stearate ($Zn(ST)_2$), benzyl ether, acetone, chloroform, 11-mercaptoundecanoic acid were all obtained from Aldrich, and used as received.

2.2 Synthesis of hexadecyl and oleyl amine modified ZnS nanoparticles

A mixture of 0.316 g $Zn(ST)_2$, 3.5 g HDA and 7 g benzyl ether were heated to 290 ^oC under N_2 flow. A 0.016 g sulfur dissolved in 2.7 g oleylamine was injected into this reaction flask. The reaction temperature was kept at 280 ^0C for 30 mins. Then the reaction flask was removed from the heating mantle and allowed to cool to room temperature. Acetone was added to precipitate the nanoparticles. The nanoparticles were further isolated by centrifugation and decantation. The as-prepared nanoparticles were redispersed in chloroform.

2.3 11-mercaptoundecanic acid ligand exchange

ZnS nanoparticles were dispersed in chloroform in a 10 mL centrifuge tube. A saturated solution of 11-mercaptoundecanoic acid (5 mL) was added, the vial was capped and sonicated for 1 hour. The solution was then centrifuged for 10 minutes at 3500 rpm and the supernatant was removed. The vial was again filled with acetone, sonicated for 5 mins and centrifuged for 10 minutes at 3500 rpm. A clear supernatant was removed. This process was repeated three times. The nanoparticles were then placed in a oven to remove the solvent. The addition of water easily disposed the particles.

2.4 Instrumentation

The photoluminescence (PL) spectra were recorded on a Fluoromax 3 fluorometer. Absolute quantum yields were determined with an excitation wavelength of 300 nm in the emission mode. The decay process of the phosphorescence was detected at a wavelength of 384 nm. After a few seconds, the excitation light source was shut off, and the phosphorescence decay intensity was collected versus time. Each experiment was repeated three times.

The XRD patterns were obtained with a diffractometer using Cu Kα radiation and employing a scanning speed of 0.02 °/s in the 2 theta range of 20° to 60°. XRD samples were prepared by evaporating a drop of concentrated nanoparticle dispersion on a silicon wafer.

The TEM images were acquired using a 200 keV Hitachi H-8000 transmission electron microscope. TEM samples were prepared by dropping 10 μl of diluted solution onto a 400 mesh carbon–coated copper grid and slowly evaporating the solvent.

^{1}H NMR spectra were obtained on a Bruker AM-360 MHz NMR instrument using 5 mm o.d. tubes. Samples were in Chloroform-d6 containing 1% TMS as an internal reference.

3. Results and discussion.

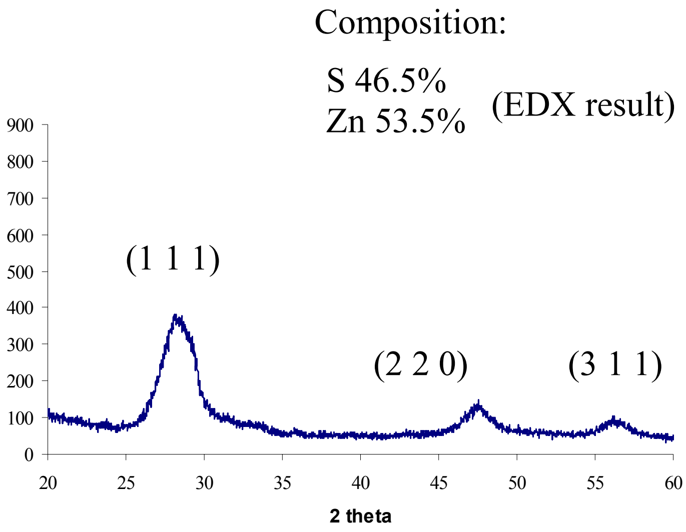

Figure 1. XRD of ZnS nanoparticles.

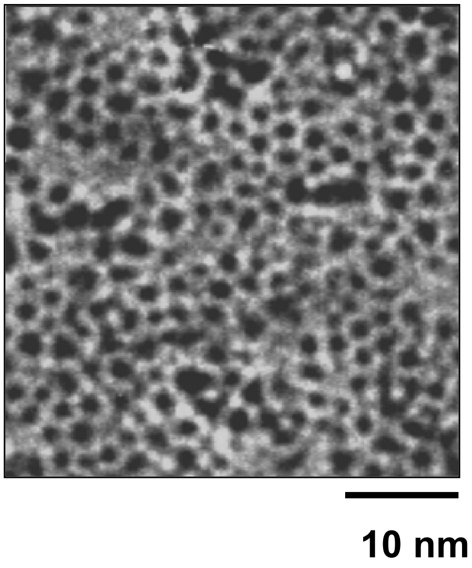

Figure 2. TEM image of ZnS nanoparticle

Fig. 1 shows the XRD pattern of the as-prepared ZnS nanoparticles. The three peaks with 2 theta values of 28.56 °, 47.82 °, and 56.58 ° correspond to the (1 1 1), (2 2 0), (3 1 1) planes of the ZnS, respectively. Those peaks position match the zinc blend crystal structure.

A TEM image of the as-prepared ZnS nanoparticles is shown in Fig. 2. The nanoparticles are spherical-shaped with an average diameter of 2 nm.

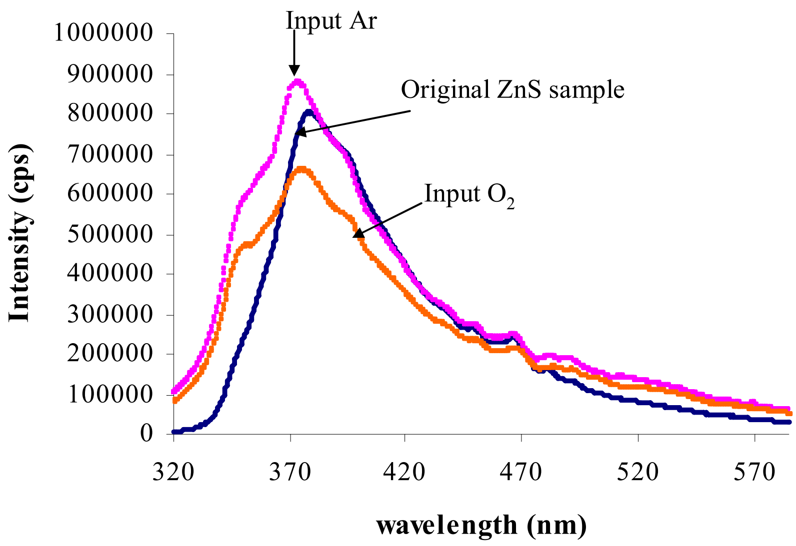

Figure 3. Fluorescence spectrum of ZnS nanoparticles with hexadecyl and oley amine ligands in chloroform.

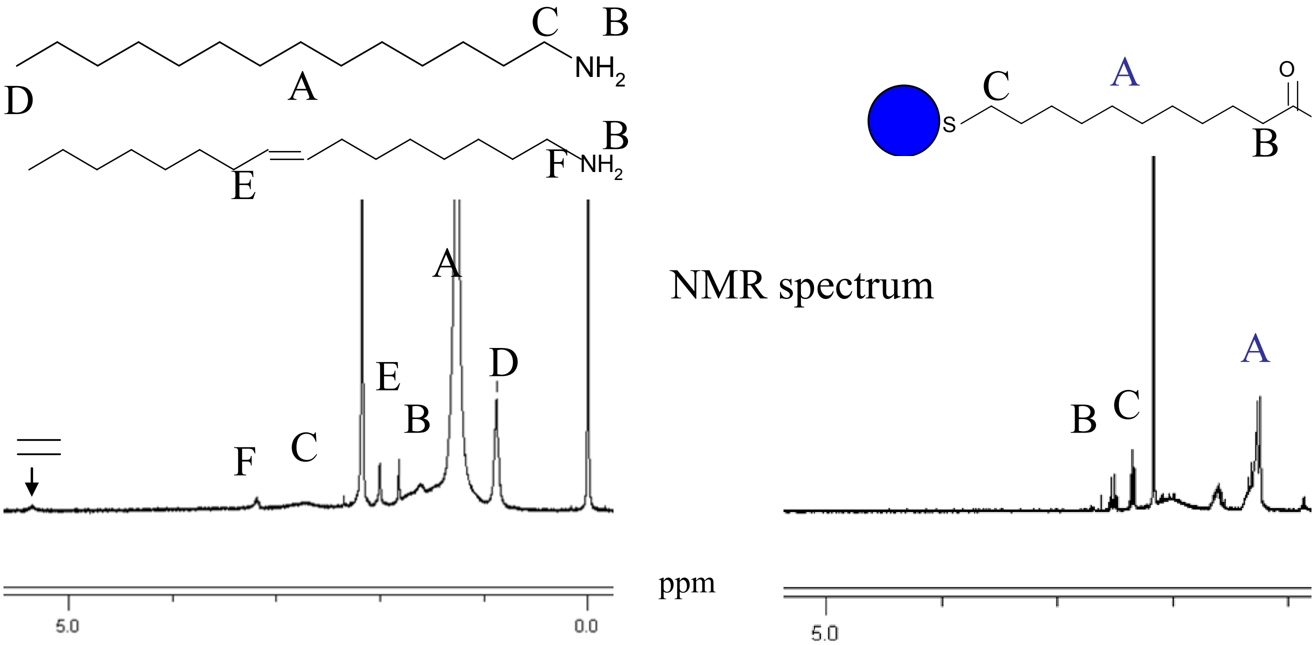

Figure 4. NMR Spectrum of ZnS nanoparticles before and after ligand exchange.

Figure 3 is the photoluminescence spectrum for the ZnS nanoparticles with oleyl amine and HDA ligand in chloroform measured using an excitation wavelength of 300 nm. A generally accepted view of the emission process in QDs is that an ekectron initial excites an electron into the conduction band of the semiconductor by ultrabandgap radiation. Emission then occurs via the relaxation of the electron or hole to a recombination center followed by radiative recombination. It was noticed that the presence of O_2 decreases the intensity of proton emission. There are three peeks at 340 nm, 370 nm and 468 nm for the sample after purging O_2 and argon. The recombination centers are due to surface state and crystal effects which lie at energy levels within the bandgap [10]. For original ZnS sample, only two peaks appear. This is caused by the coupling of the surface energy state and surface defect state, which make the luminescence peaks overlap. After purging with Ar, the intensity of luminescence intensity increases, while after purging with oxygen, the intensity decreases. It can be explained by the following quantum yield equation [11].

$$I_e \approx \phi_e = \frac{k_r}{k_r + k_{nr} + k_q[quencher]} \tag{7}$$

Here, I_e is the fluorescence intensity of an excited state. ϕ_e is the emission quantum yield, the radiative (k_r) and non-radiative (k_{nr}) decay rate constants are intrinsic properties to the excited state molecule, whereas k_q is the quenching rate constant. As the quencher oxygen concentration increases, the fluorescence intensity decreases

During preparation of the ZnS nanoparticles, they are capped with hexadecylamine and oleylamine. These ligand's amine groups attached to the nanoparticle surface and thus the alkyl groups make the nanoparticles hydrophobic. In most situations, oxygen is dissolved in water. The synthesized nanoparticles which are insoluble in water is a clear limitation for environmental applications. In our experiments, water soluble ZnS QDs are prepared using 11-mercaptoundecanic acid ligand exchange. From NMR spectrum (figure 4), the original peaks of hexadecyl and oleyl amine proton peaks are replaced by 11-mercaptoundecanoic.

The photoluminescence spectrum for the ZnS nanoparticles with 11-mercaptoundecanoic acid ligand in water solution was measured using an excitation wavelength of 300 nm. It displays a strong peak at 338 nm, 384 nm, and a small peak at 468 nm (figure 6). The spectrum shape of ZnS with the MUA ligand is quite different than with the long chain amine ligand. This may be caused by different trap states on the surface of the nanoparticle leading to the appearance of different emission bands [12]. When the particle dimensions are small enough, the semiconductor nanoparticles have large surface-to-volume ratios that lead to enhanced optical detectability of surface effects [13]. Some theoretical attempts to predict semiconductor properties from a quantum mechanical basis have recognized the importance of the surface [14]. We assume the peak at 436 nm is caused by the interstitial lattice defects. The peak around 384 nm may be attributed to surface defects. The photo-generated electrons can be trapped into sulfur vacancies on the surface through a nonradiative decay and recombination with a hole in the valence band of ZnS, resulting in this 384 peak. The peak around 338 nm is related to surface states. The ions accumulated on the surface are thought to create energy levels within the bandgap of the semiconductor which act as centers for

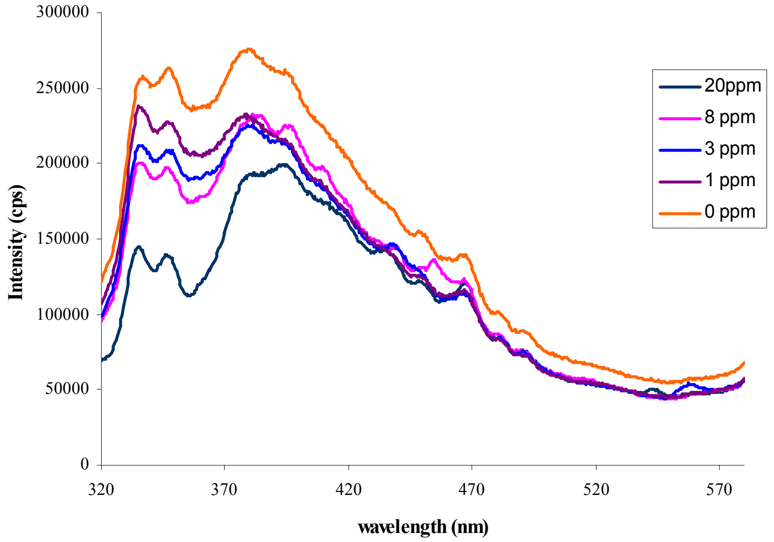

Figure 5. Fluorescence spectrum of ZnS nanoparticles with MUA in water dispersion containing various amounts of dissolved oxygen. The higher the dissolved oxygen concentration, the lower the emission intensity of the nanoparticles.

recombination of the electron /hole pairs.

According to the Stern-Volmer relationship, the luminescence intensity can be directly related to the oxygen concentration assuming that the exited state is only quenched by dissolved oxygen [10].

$$\frac{I_0}{I} = 1 + K_{sv}[O_2] \qquad (5)$$

Here, K_{sv} is the Stern-Volmer quenching constant, I and I_0 are the measured quenched and unquenched emission intensities, respectively. $[O_2]$ is the dissolved oxygen concentration.

The accuracy of the intensity based measurements in real-world applications is not very good. It can be confounded by several factors: excitation intensity, light losses in optical fibers, photo-bleaching, and changes in the light scattering and sample absorption characteristics. Frequent recalibration and other corrections are thus required. Instead of using luminescence intensity, the lifetime of the lumophore's decay process can be measured. The lumophore decay process is also described by a Stern-Volmer equation [10]:

$$\frac{\tau_0}{\tau} = 1 + k\tau_0[O_2] \qquad (6)$$

Where τ and τ_0 are the quenched and unquenched excited state lifetimes, respectively, and k is the diffusion-dependent quenching constant. By measuring either the lifetimes or the emission intensities, the dissolved oxygen concentration can be determined

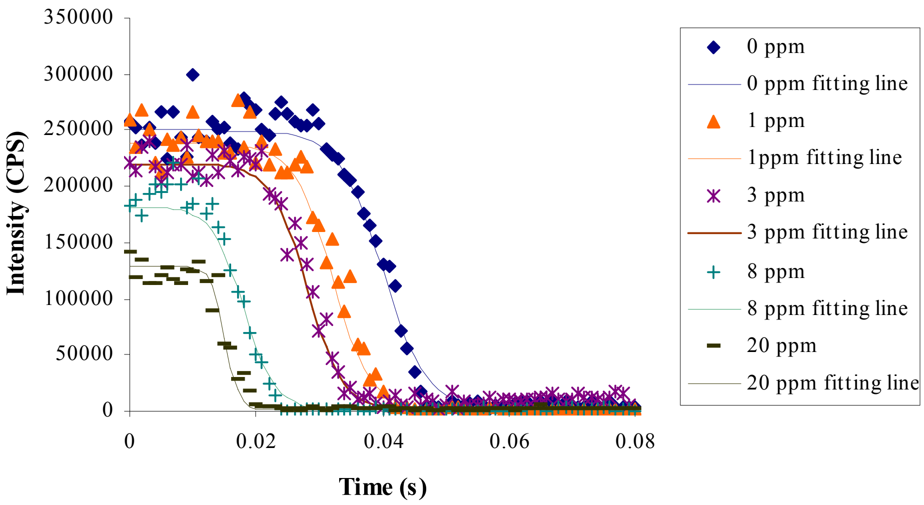

Figure 6. Decay process of ZnS nanoparticle in water dispersion with different dissolved oxygen concentrations.

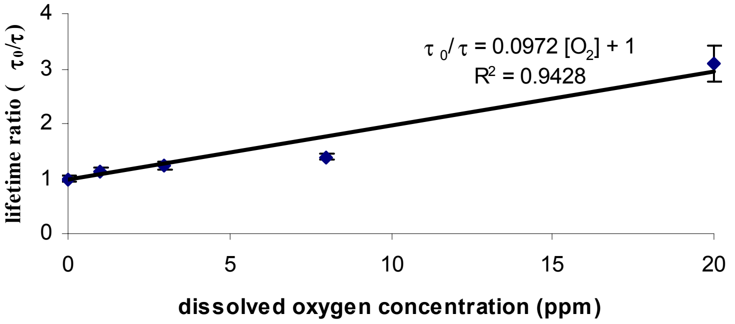

Figure 7. Lifetime ratio with different dissolved oxygen concentration

The luminescence decay rate of ZnS nanoparticles with MUA at different dissolved oxygen concentration was measured with the fluorometer at 338 nm at which the peak is most sensitive to the oxygen change. The observed fluorescence decay theory is complex. It is affected by the rate of recombination of trapped electrons and holes and the distance between the traps. The time dependence of the emission from CdS QDs has been studied by several investigators. They have found the decay to be complex and to depend on the excitation intensity due to the biomolecular nature of the recombination process [15]. In our measurements, the decay data given in figure 7 were fitted to a sigmoid function [16]. The calculated value of τ are plotted as τ_0/τ versus the dissolved concentration (fig. 8) The data were then fitted to a straight line with a fixed intercept of 1.0. The slope of this line is 0.097. The results are in good agreement with the Stern -Volmer equation.

Conclusions

ZnS nanocrystrals are synthesized with oleylamine and hexadecylamine using zinc stearate and elemental sulfur as the precursors and then made water soluble by adding MUA ligand. It was shown that dissolved oxygen concentration affects the ZnS nanoparticles' fluorescence spectrum. Relation of the lifetime ratio with different dissolved oxygen has a good fit to the linear Stern–Volmer equation.

Acknowledgements

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